Seminar Paper No. 009

PB193153

Selected Papers
from the
BUREAU of
RADIOLOGICAL HEALTH
Seminar Program

PROPERTIES of LIQUID CRYSTALS and THEIR APPLICATION to the MEASUREMENT of MICROWAVES and INFRARED RADIATION

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
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27

This paper was edited and prepared under the supervision of A. Burt Kline, Jr., Seminar Program Officer, Office of Information, Bureau of Radiological Health.

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SELECTED PAPERS from the BUREAU of RADIOLOGICAL HEALTH SEMINAR PROGRAM

FOREWORD

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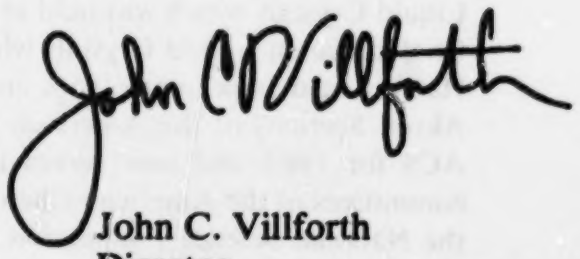
I encourage the readers of these reports to inform the Bureau of their opinions of these papers and of their value to the radiological health community.



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Glenn H. Brown is a native Ohioan who holds a B.S. degree from Ohio University and a Ph.D. from Iowa State University. He has taught at the University of Mississippi, Iowa State University, University of Vermont, University of Cincinnati and has been at Kent State University since September 1960. At Kent State Dr. Brown is Director of the Liquid Crystal Institute and Regents Professor of Chemistry.

He is the author or co-author of numerous papers in scientific journals, six books and two patents. The scientific papers are quite diverse and cover the general subjects of polarography, conductance of solutions, viscosity of solutions, liquid crystals, liquid dielectrics, structure of liquids and concentrated solutions, and photochromism. His present research interests include liquid crystals, structure of concentrated salt solutions and phtochromism.

Some of the organizations of which Dr. Brown is a member are the American Chemical Society, American Association for the Advancement of Science, Sigma Xi, Phi Lambda Upsilon, Alpha Chi Sigma, American Institute of Chemists, the Ohio Academy of Science, and the New York Academy of Science.. He was president of the Ohio Academy of Science in 1960. In the summer of 1965 he was chairman of the First International Conference on Liquid Crystals which was held at Kent State University. He chaired the Second International Conference on Liquid Crystals which was held August 12-16, 1968 at Kent State University. He was held important offices and committee assignments in the Memphis, Cincinnati and Akron Sections of the American Chemical Society. He was chairman of the Akron Section ACS for 1965 and now serves as Councilor from the Section. Dr. Brown has served on committees of the American Chemical Society at the National level and on advisory panels for the National Science Foundation. He was General Chairman for the Central Regional ACS meeting held in Akron, May 9-10, 1968.

Dr. Brown is editor of the journal MOLECULAR CRYSTALS AND LIQUID CRYSTALS.

PROPERTIES OF LIQUID CRYSTALS AND THEIR APPLICATION[1] TO THE MEASUREMENT OF MICROWAVES AND INFRARED RADIATION

Before we look at the application of liquid crystals to the measurement of microwaves and of infrared radiation, we shall consider some properties of this interesting state of matter. Knowing something about the properties of liquid crystalline materials, we can appreciate and understand the applications which will be discussed and extend the field of applications by developing new ones.

Liquid crystals are divided into two major classes. One of these is identified as **thermotropic** liquid crystals which as the name implies are prepared by heating compounds. The known thermotropic liquid crystals are organic compounds. A few coordination compounds containing mercury (II) have been synthesized, e.g. bis-(p-methylbenzal)-p,p'-diamino mercury biphenyl. **Lyotropic** liquid crystals constitute the second broad category of liquid crystals. These systems are prepared by mixing two or more components. In water systems the second component is generally an amphiphile; water systems may be multicomponent. This is true for nonaqueous systems. Lyotropic systems can be large in number and varied in composition. Thermotropic liquid crystals have received a wider publicity than lyotropic ones, but that relationship will very likely be reversed in the near future. Since the applications we propose to discuss involve thermotropic liquid crystals we shall consider only this class.

Thermotropic liquid crystals have been classified under three categories based on their optical properties. The **nematic** liquid has spontaneous orientation of the molecules along their axes. We now know the structure that was, for many years, identified as cholesteric is a special case of the nematic. **Smectic** liquids have arrangement of molecules in layers which give them a stratified structure; they are subdivided into several textures. Characteristic properties of thermotropic liquid crystalline structures may be summarized in tabular form as done in Figure 1. Various aspects of these properties will be presented.

Molecular Geometry For Molecules Which Form Thermotropic Liquid Crystals

We shall take a brief excursion into the molecular geometry of thermotropic liquid crystals. We have reached the "state of the art" where we can make some general predictions about the qualifications a molecule must have if it is to show liquid crystallinity. These may be summarized in a general way as follows:

1. **Spatial Effects**
   (a) The molecule will be elongated and rectilinear. If the molecule has "flat" segments (e.g. benzene rings) liquid crystallinity is often enhanced.
   (b) The molecule should not have minimal internal free rotation.

2. **Energy Effects**
   (a) Simultaneous existence of strong dipoles and easily polarizable groups in the molecule seem essential.
   (b) The most pronounced liquid crystalline effect generally occurs if the strong dipole is on the molecular axis.
   (c) Easily rotated polar groups at the end of the molecule are of subordinate importance.

[1]This paper was presented as part of the National Center for Radiological Health's (now the Bureau of Radiological Health) Seminar Program on March 14, 1969 in Rockville, Maryland.

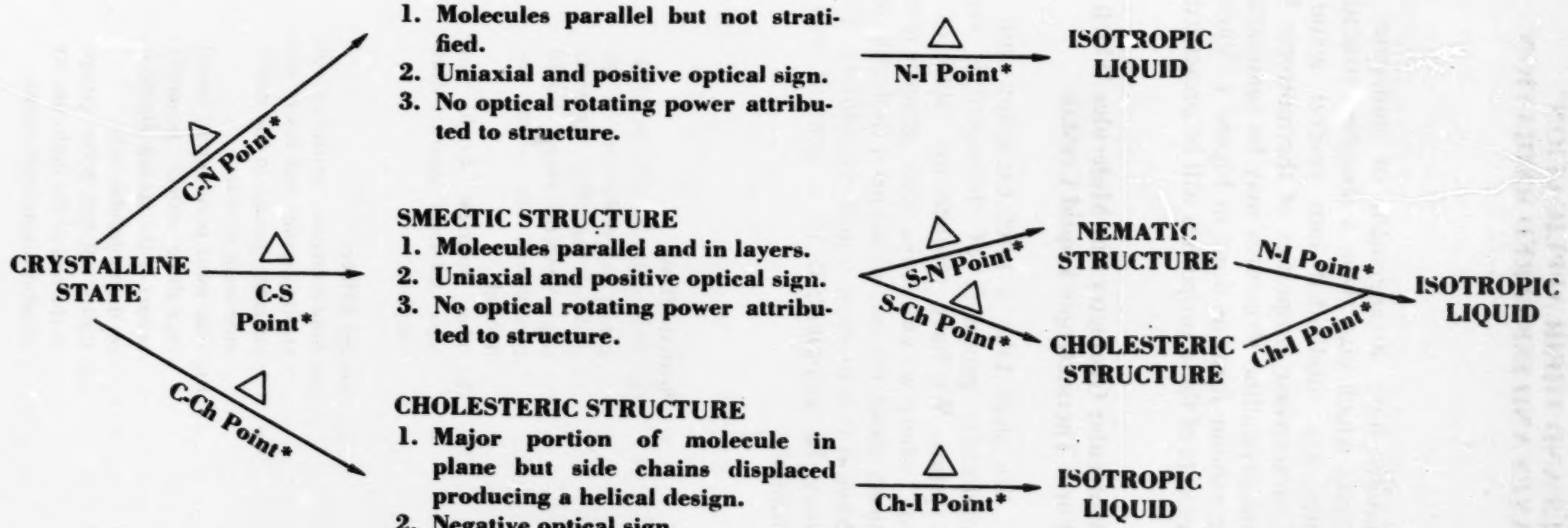


Figure 1. Relationship among stability ranges of crystalline, liquid crystalline and liquid states. Nomenclature for transition temperatures is designated on arrows.

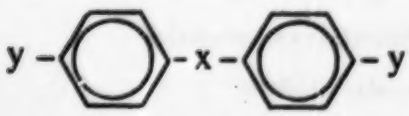
***Key:**

C-N	Point:	Crystal-Nematic transition temperature
C-S	Point:	Crystal-Smectic transition temperature
C-Ch	Point:	Crystal-Cholesteric transition temperature
S-N	Point:	Smectic-Nematic transition temperature
S-Ch	Point:	Smectic-Cholesteric transition temperature
N-I	Point:	Nematic-Isotropic transition temperature
Ch-I	Point:	Cholesteric-Isotropic transition temperature

Of the criteria cited, the absence of internal free rotation is probably the most important one. Reduction or elimination of free rotation is often accomplished by building double or triple bonds along the molecular axis.

Examples of typical molecules forming liquid crystals

A typical molecule containing aromaticity which shows liquid crystallinity on heating may be represented by the general formula:



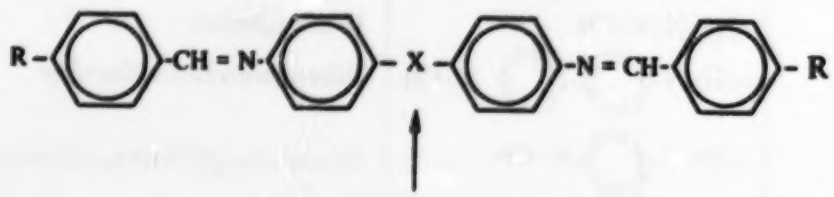
An illustrative list of units which can take the place of x in the molecule is compiled in Table 1. A typical example of each type is included. For convenience, the table is divided into symmetrical and unsymmetrical molecular structures. Types of end groups, y, are summarized in Table 2. The terminal groups may be alike or unlike. Neither of these tables is meant to contain an exhaustive listing of all the groups which have been reported. It should be further emphasized that the molecular unit chosen is only one of many general types known. A large list of thermotropic liquid crystals may be found in Landolt-Börnstein. **(1)**

A general pattern of molecular structures which show liquid crystallinity may be drawn from the compilation in Table 1. Molecular structures which form liquid crystals often consist of two or more benzene nuclei joined by groupings of two (or a multiple of two) atoms. There are generally one or more multiple bonds along the molecular axis. Compounds in which benzene rings are joined by a single atom or by a chain containing an odd number of atoms show little, if any, tendency toward liquid crystallinity. Common examples of such compounds are derivatives of diphenyloxide and diphenylmethane.

The effect of atomic arrangements within a molecule can alter intermolecular attractions which, in turn, alter the properties of liquid crystals (e.g. transition temperatures). The reader is referred to the review article by Brown and Shaw for details on this subject. **(2)**

Influence of central and end groups on transition temperatures

Figure 2 gives an illustrative representation of the effect of the central and end groups on the nematic-liquid point for two series of compounds with the basic structure:



The end group (R) in one case is non-polar and in the second case polar. The data in Figure 2 exemplify the general rule that for any given basic molecular structure, and for a given central group, an increase in the polarity of the end group decreases the nematic-liquid point.

The alkylbenzoic acids and the alkoxybenzoic acids furnish an interesting series of compounds for comparison of change of smectic-nematic and nematic-liquid points in an homologous series. These plots are representative of most homologous series that have been studied. In ascending a homologous series, the following general statements may be made:

1. **The nematic-liquid transition temperatures usually fall.**
2. **Smectic-nematic transition temperatures rise quickly at first and then more gradually with increasing alkyl chain length.**
3. **Smectic-liquid transition temperatures often rise to a maximum in the lower homologues and then fall steadily.**

These points are illustrated in Figure 3.

Table 1. Composition of central group in aromatic type molecules showing the mesomorphic state

Symmetrical molecules

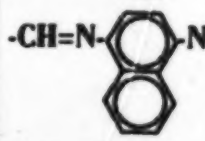
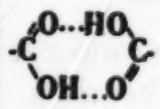
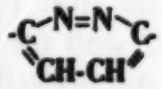
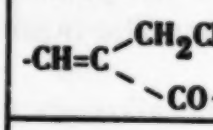
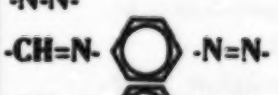
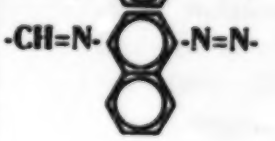
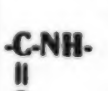
x = Central Group	Type	Typical Example
-CH_2-CH_2-	Dibenzylideneaminodibenzyl	4,4'-Di (p-methoxybenzylideneamino) dibenzyl
-CH=CH-	trans-Diphenylethylene	p,p'-Diacetoxystilbene
-C≡C-	Diphenylacetylene	1,2-Di-(p-methoxyphenyl) Acetylene
-N=N-	trans-Azobenzene	p-(p-Acetoxyazo) benzoic acid
-CH=CH-CH=CH-	Diphenylbutadiene	1,4-Di-(p-Methoxyphenyl) Butadiene
-CH=N-N=CH-	Dibenzalazine	p,p'Dimethoxybenzalazine
	Dibenzaldiphenyldiamine	Dibenzalbenzidene
	Dibenzalnaphthalenediamine	p,p'-Dimethoxydibenzal-1,4 Naphthalenediamine
	Carboxylic acids (double molecule)	p-n-Butylbenzoic acid (double molecule)
	Diphenylpyridazine	p,p'-n-Butyldiphenylpyridazine
	Dibenzalcyclopentanone	p,p'-Diethoxybenzalcyclopentanone
Unsymmetrical molecules		
-CH=N-	Benzalaniline	p-(p-Cyanobenzal) anisidine
	Phenyl ester of benzoic acid	p-(p-Methoxybenzoxy) benzoic acid
	Azoxybenzene	p-Azoxyanisole
	Benzal-p-aminoazobenzene	Anisal-p-aminoazobenzene
	Benzal-l-aminonaphthalene-4-azobenzene	Anisal-l-naphthylamino-4-azobenzene
	p-benzanilide azomethine derivative	p-carboxyl-p'-4-methoxybenzyldineamino-benzanilide
-NH-CH-	Azomethine-N-phenylbenzyl-amine derivative	4,4'-Di(p-methoxybenzylideneamino)-N-phenylbenzyl amine

Table 2. Composition of end group in aromatic type molecules showing the mesomorphic state

y = End Group	Type	y = End Group	Type
$CH_3(CH_2)_n$-	Normal alkyl	$CH_3(CH_2)_nOCO$-	Alkyl carboxylic acid esters
$(CH_3)_2CH(CH_2)_n$-	Branched alkyl	$C_6H_5(C_6H_4)_nOCO$-	Aryl carboxylic acid esters
$CH_3(CH_2)_nO$-	Alkoxy	CN-	Cyano
$CH_3O(CH_2)_nO$-	Oxygen-broken alkoxy	NO_2-	Nitro
Cl, Br, I	Halogen	NH_2-	Amine, substituted amine

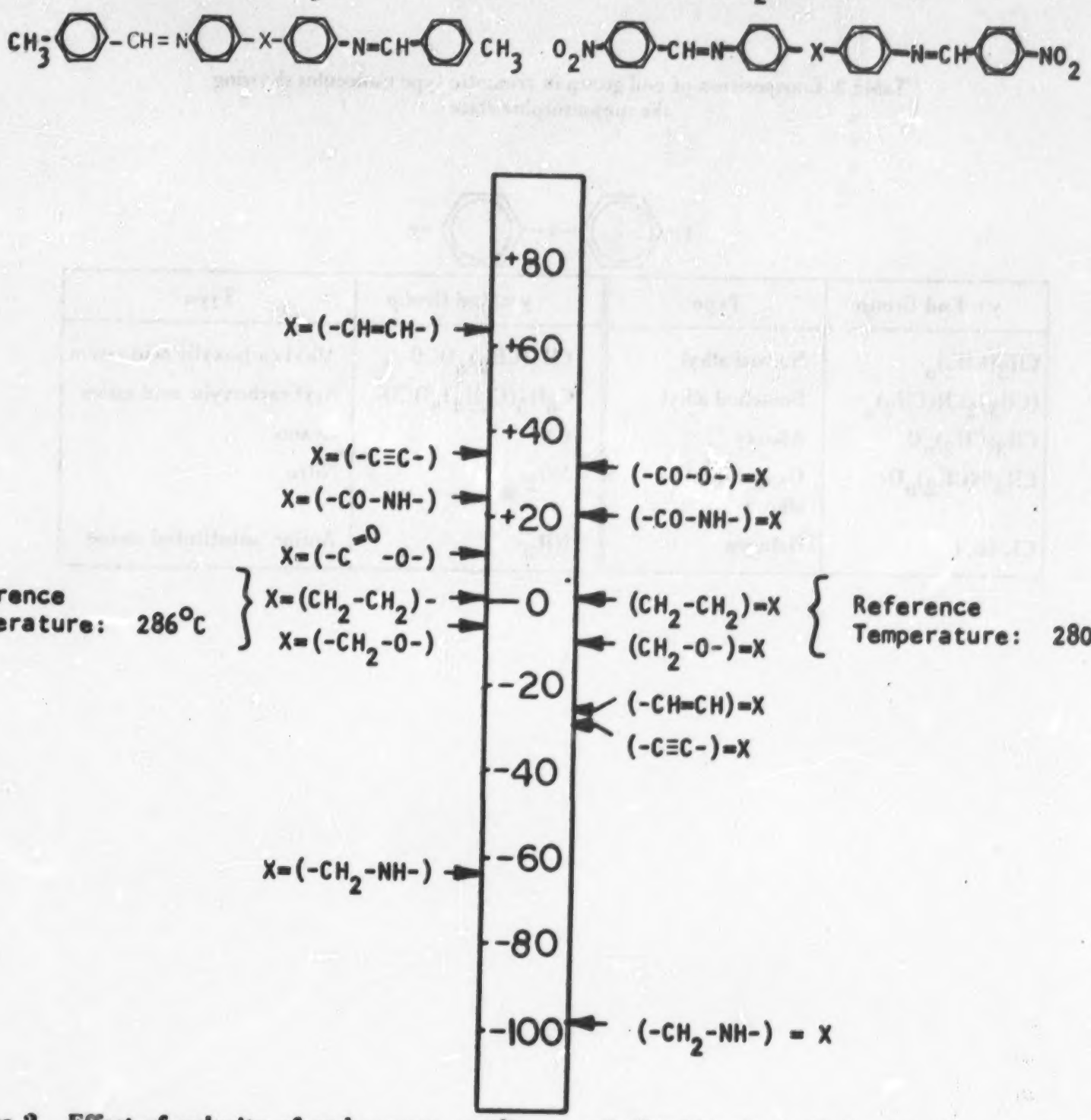


Figure 2. Effect of polarity of end groups on the nematic-liquid point; effect of change of central group on the nematic-liquid point.

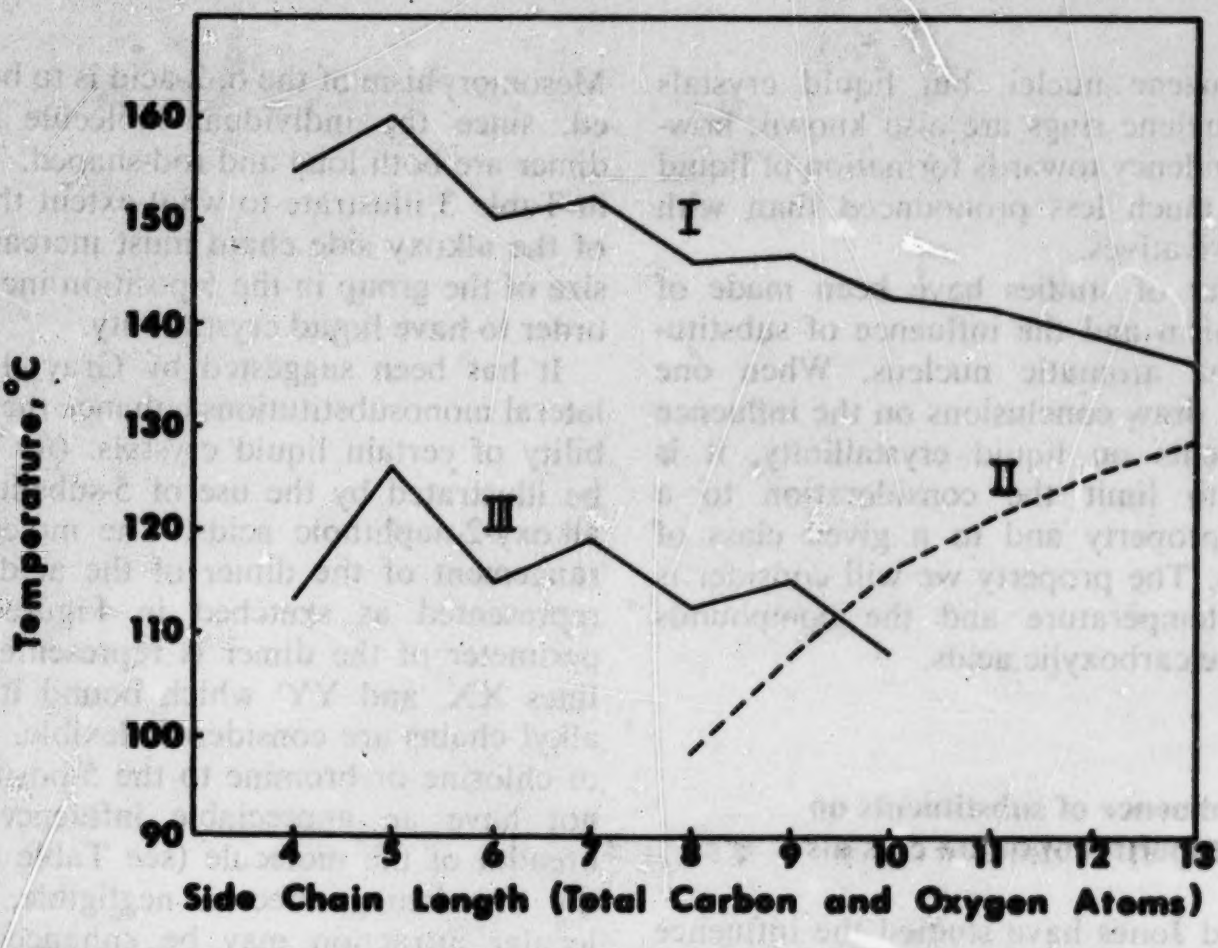
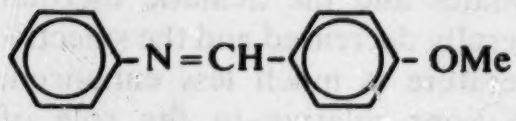
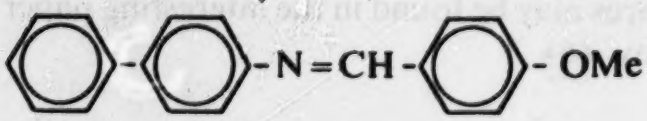


Figure 3. Curve I, nematic-liquid point for the p-n-alkoxybenzoic acids (Gray and Jones (3)). Curve II, smectic-nematic points for p-n-alkoxybenzoic acids (Gray and Jones (3)). Curve III, nematic-liquid points for p-n-alkylbenzoic acids (Weygand and Gabler (4)). 4 = n-butyl, etc., for alkyl groups and 4 = n-propoxy, etc., for alkoxyl groups.

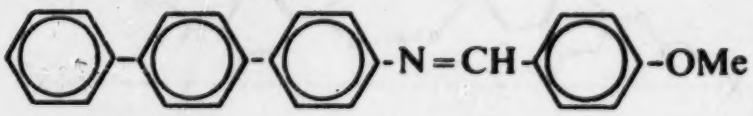
Molecular length can also be added by the use of benzene rings. The tendency to form liquid crystals increase with the number of aromatic nuclei in the molecule, provided they are linked in para positions. The effect of adding, aromatic rings can be illustrated by the following examples:



non-mesomorphic



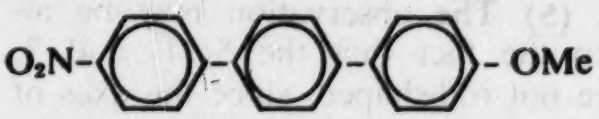
mesomorphic



mesomorphic

non-mesomorphic

non-mesomorphic



mesomorphic

With three and four benzene rings (ter- or quater-phenyl), elongated substituents in the para-positions of the end nuclei are no longer necessary; nitro- or amino- groups are sufficient to induce mesomorphism. Most aromatic compounds which show liquid-crystallinity

contain benzene nuclei, but liquid crystals with naphthalene rings are also known; however, the tendency towards formation of liquid crystals is much less pronounced than with benzene derivatives.

A number of studies have been made of mesomorphism and the influence of substituents on the aromatic nucleus. When one attempts to draw conclusions on the influence of substituents on liquid crystallinity, it is necessary to limit the consideration to a particular property and to a given class of compounds. The property we will consider is transition temperature and the compounds will be some carboxylic acids.

Influence of substituents on properties of liquid crystals

Gray and Jones have studied the influence of substituents on the properties of the alkoxybenzoic acids and the alkoxynaphthoic acids. (5) Compounds presented in Table 3 illustrate the effect of change of substituent in the 3-substituted alkoxybenzoic acids. One can observe that an increase in separation of the molecules brought about by the increase in size of the halogen atom results in a decrease and finally the eventual loss of liquid crystallinity in this acid series. The length of the side chain at which the nematic and smectic structures appear increases as the size of the atom in the 3-position increases (see Table 3).

Gray and Jones also found that the unsubstituted 4- and 5-n-alkoxy-1-naphthoic acids and the 6-n-alkoxy-2-naphthoic acids are mesomorphic. (5) The observation may be attributed to the fact that the 5, 1- and 7, 2-acids are not rod-shaped, since the axes of the carboxyl and alkoxy groups are not in line; this is especially true when the dimer (the form in which these acids exist at the molecular level) is considered. The 4, 1-acid is essentially linear but is also very broad. If the dimer form exists, the two naphthalene rings may cause such imbrication in the molecule that the closest packing in the crystal lattice is not one in which the molecules lie parallel. Mesomorphism of the 6, 2-acid is to be expected, since the individual molecule and the dimer are both long and rod-shaped. The data in Table 3 illustrate to what extent the length of the alkoxy side chain must increase as the size of the group in the 5-position increases in order to have liquid crystallinity.

It has been suggested by Gray that some lateral monosubstitutions enhance thermal stability of certain liquid crystals. (6) This can be illustrated by the use of 5-substituted-6-*n*-alkoxy-2-naphthoic acids. The molecular arrangement of the dimer of the acid may be represented as sketched in Figure 4. The perimeter of the dimer is represented by the lines XX′ and YY′ which bound it and the alkyl chains are considered flexible. Addition of chlorine or bromine to the 5-position does not have an appreciable influence on the breadth of the molecule (see Table 3). Since the broadening effect is negligible, intermolecular attraction may be enhanced by the increased dipole from the presence of the chlorine or bromine. This effect should be more pronounced for the smectic structure. This is the case. The addition of iodine broadens the molecule and, as a consequence, the nematic-isotropic point is lowered and the smectic-nematic point is not enhanced to the same degree as with chlorine and bromine. One can conclude that those substituents which fill gaps in a molecule will have most influence on smectic stability in that they generally result primarily in change in dipole. If the substituent broadens the molecule, that property often predominates and the nematic thermal stability is generally decreased and the smectic-nematic temperature is much less enhanced. Further correlations relative to the role of substituents on stability of smectic and nematic structures may be found in the interesting paper by Gray. (6)

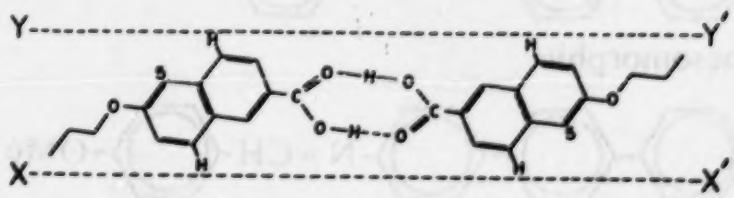


Figure 4. Representation of the dimer of a 6-n-alkoxy-2-naphthoic acid.

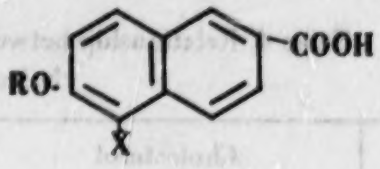
Table 3. Influence of substituents on the mesomorphism of alkoxybenzoic and 6-alkoxy-2-naphthoic acids

Gray and Jones (5a, 5b, 6)

Alkoxybenzoic acids, RO-C$_6$H$_3$(X)-COOH

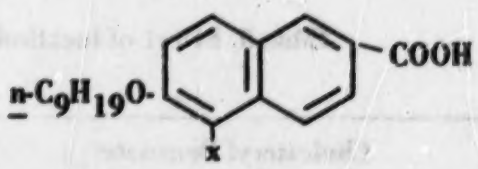
X	Length of n* at First Appearance of				
	Nematic structure	Smectic structure	Smectic structure only	Maximum phase length °C	Value of n* at maximum phase lengths
H.....	3	7	18	57	10
F.....	8	9	16	16	16
Cl.....	8	8	..	4.5	16

6-Alkoxy-2-naphthoic acids,



X	Length of n* at First Appearance of				
	Nematic structure	Smectic structure	Smectic structure only	Maximum phase length °C	Value of n* at maximum phase lengths
Cl.....	3	6	16 and 18	42	6
Br	3	7	16 and 18	40	7
I	4	8	16 and 18	25	8
NO_2...	9	12	....	1.5	10

5-Subetituted-6-n-nonyloxy-2-naphthoic acids,



X	Smectic-Nematic Point, °C	Nematic-Isotropic Point, °C
H.....	140	183.5
Cl.....	185.5	194.5
Br.....	180	192.5
I.....	157.5	182

*n = number of carbon atoms in alkoxy side chain

The effect of polyfluorination on benzene rings has been observed in a couple of recent studies. Goldmacher and Barton showed that polyfluorination that resulted in polylateral substitution of an elongated molecule leads to greater thermal stability than one would predict. (7) In some cases the thermal stability exceeds that of the unsubstituted compound and the smectic system is especially enhanced.

Cholesteric liquid crystals

Before leaving this section we should consider, even though briefly, the influence of molecular structure on the properties of cholesteric liquid crystals. Cholesteryl nonanoate is sketched in Figure 5. One way to study the thermal stability of a cholesteric liquid crystal is to modify the sterol skeleton. Wiegand made such studies on the benzoate esters of cholesterol and epicholestanol. (8) He considered the change in the position of the double bond in cholesterol and of the two double bonds in cholestadienol. These data are collected in Tables 4 and 5.

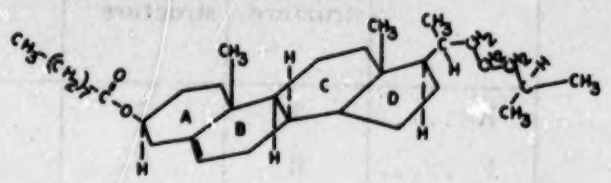


Figure 5. Formula for cholesteryl nonanoate.

Table 4. Relationship between spatial structure and mesomorphic character of cholesteryl derivatives Wiegand (8)

Ester	Cholesterol		Cholestanol		Epicholestanol	
	Crystal-nematic point	Nematic-liquid point	Crystal-nematic point	Nematic-liquid point	Crystal-nematic point	Nematic-liquid point
	°C	°C	°C	°C	°C	°C
Benzoyl	149 -150	178	136.5-137	155	104 -105	No nematic structure
Anisyl	162.5-163	236	160 -160.5	239	104.5-106	No nematic structure
4-Phenylbenzoyl	177 -179	290	171 -172	291	115 -117	No nematic structure
4-Toluyl	179.5-180.5	241	171.5-172.5	225	91.5- 92.5	No nematic structure
2-Toluyl	120 -121	133	122 -123	(108)	96 - 98	No nematic structure

Table 5. Effect of location of double bonds in cholesteryl derivatives Wiegand (8)

Cholesteryl Benzoate			Cholestadienyl Benzoate		
Location of double bond	Crystal-nematic point	Nematic-liquid point	Location of double bond	Crystal-nematic point	Nematic-liquid point
	°C	°C		°C	°C
5,6	149-150	178	5,6; 7,8	142.5-143	188
7,8	157-158	176	6,7; 8,9	146	180
8,9	147	174	7,8; 14,15	149-150 (m.pt.)	None
8,14	115	140	8,9; 24,25	126-128	138
14,15	169-171	None	14,15; 24,25	120-122 (m.pt.)	None

It is obvious that changes in the sterol skeleton alter the cholesteric-isotropic point, but it is difficult to draw significant conclusions because the molecules are so complex. If one modifies the ester group on the A ring of cholesterol, one finds that the short alkyl chains favor cholesteric behavior and longer alkyl chains give, in addition, smectic properties. (9) Chain branching lowers the transition temperatures. (10)

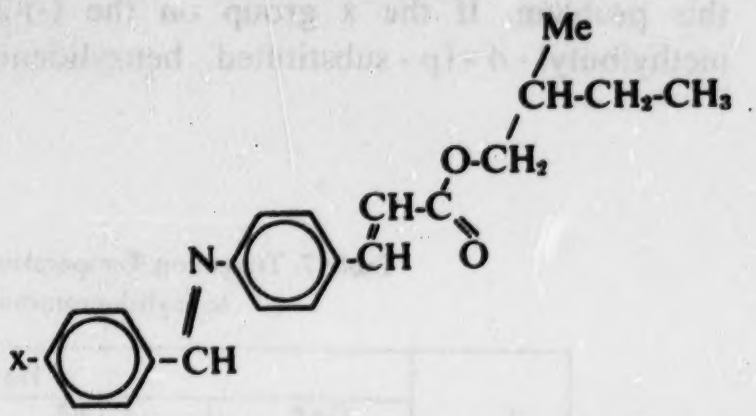
The substituted cholesteryl benzoates give some interesting properties. Substitution in the o- or m-positions in the benzene ring of the ester lowers the cholesteric-isotropic transition temperature while p-substitution raises this transition temperature. Group efficiency for p-substitution derived from the literature is as follows: (11, 12)

Substituent: Phenyl > NO_2 > NH_2 > Me > MeO > H

Cholesteric-Isotropic point °C: 290 265 250 241 236 178.5

The stability order suggests a similarity between cholesteric and nematic states.

Gray has made some interesting observations on the thermal stability of cholesteric phases which are prepared from compounds that are not derivatives of cholesterol. (6) He has chosen the derivatives of (-)-2-methylbutyl-4- (p-substituted benzylideneamino) cinnamates. The basic molecular unit is:



Transition temperatures of the (-)-2) methylbuty 1 - 4 (p - n - alkoxybenzylideneamino) cinnamates are collected in Table 6. Only the methoxy group gives a compound that shows cholesteric properties. This corre-

Table 6. Transition Temperatures for (-)-2-Methylbutyl-4-(p-n-alkoxybenzylideneamino) cinnamates (from Gray[6])

n-Alkoxy	Transition Temperature (°C)		
	C-S* Point	S-Ch* Point	S-I* or Ch-I* Point
MeO	54	76.5	98
EtO	75.5	----	124.5
PrO	86.5	----	120.5
BuO	84	----	126.5
PnO	64	----	120
HxO	60.5	----	122.5
HpO	74	----	117
OcO	73.5	----	118

*Key

C-S Point: Crystal-Smectic Transition Temperature
S-Ch Point: Smectic-Cholesteric Transition Temperature
S-I Point: Smectic-Isotropic Transition Temperature
Ch-I Point: Cholesteric-Isotropic Transition Temperature

sponds to the properties observed for a comparable series of alkoxy esters of the same molecular skeleton, but with the 2-methylbutyl group replaced by an ethyl group. The ethyl ester is non-cholesteric, but the nematic transition disappears early in the homologous series just as is observed with the cholesteric-type cinnamates.

We will consider only one other aspect of this problem. If the x group on the (-)-2-methylbutyl - 4 - (p - substituted benzylidene-amino) cinnamates is changed to a variety of groups, some interesting results are found. Transition temperatures on these compounds are presented in Table 7. It is interesting to note that not all of these compounds are cholesteric even though they are all active esters. The nitro- and cyano-compounds are enantiotropic liquid crystals and exhibit all properties expected of the cholesteric structure. They reflect light which changes from red to blue on cooling.

Table 7. Transition Temperatures for (-)-2-Methylbutyl-4-(p-substituted-benzylideneamino) cinnamates (from Gray[6])

X	Transition Temperature (°C)				
	C-S* Point	C-Ch* Point	S-Ch* Point	S-I* Point	Ch-I* Point
NMe_2	96	---	---	125	---
Me	78	---	---	84	---
MeO	54	---	76.5	---	98

X	Transition Temperature (°C)		
	C-I* Point	C-Ch* Point	Ch-I* Point
CN	----	93.5	108
NO_2	----	82.5	84
Br	84.5	----	64.5**
F	72	----	<<45**
H	56.5	----	----

*Key

C-S Point: Crystal-Smectic Transition Temperature
C-Ch Point: Crystal-Cholesteric Transition Temperature
S-Ch Point: Smectic-Cholesteric Transition Temperature
S-I Point: Smectic-Isotropic Transition Temperature
Ch-I Point: Cholesteric-Isotropic Transition Temperature
C-I Point: Crystal-Isotropic Point

**Monotropic Cholesteric State

The data in Table 7 may be used to establish a terminal group efficiency order. Using data from Table 7 and from Gray the order of thermal group effiency may be represented as follows: **(13)**

1 4-(p-substituted benzylideamino)-4'-methoxybiphenyl

Nematic: MeO > NO_2 > Cl > Br > H

4'-substituted biphenyl-4-carboxylic acids

Nematic: CN > MeO > Cl > H

(-)2-methylbutyl-4-(p-substituted benzylideamino) cinnamates

Cholesteric: CN > MeO > NO_2 > Cl > Br > H

4-(p-substituted benzylideamino)-4'-n-octyloxybiphenyls

Smectic: Br > Cl > H > NO_2 > MeO

Cholesteryl p-substituted benzoates

Cholesteric: Ph > > MeO ≈ NO_2 > Cl > Me > H

Note that the efficiency orders for the nematic and cholesteric phases are identical which shows strong evidence for the close relationship between the nematic and cholesteric structures. The terminal efficiency order for the smectic phase is quite different from the other two. The substituted cholesteryl benzoates follow the pattern of the (-)-2-methylbutyl - 4 - (p-substituted benzylideneamino) cinnamates.

Further correlations of nematic and cholesteric liquid crystals can be found by checking papers by Cano and by Leclerq, Billard and Jacques. **(14, 15, 16)**

Aliphatic compounds that form liquid crystals

The number of aliphatic compounds that exhibit liquid crystallinity is not nearly so large as that of the aromatic type. The monocarboxylic aliphatic acids and their salts are the most commonly encountered aliphatic compounds showing mesomorphism. The simplest aliphatic compound that shows mesomorphism is 2,4-nonadienoic acid. This compound has a crystal-nematic point of 23°C and a nematic-liquid point at 49°C. In this compound the polarizability of the double bonds raises the intermolecular attractions to such a level that mesomorphism occurs.

OPTICAL PROPERTIES OF LIQUID CRYSTALS

Microscopic observations: Many transparent materials, while homogeneous, are optically anisotropic, that is, the velocity of light waves in them is not the same in all directions. Materials having this property are said to be doubly refracting, or birefringent. When ordinary light which vibrates in all directions strikes the surface of a birefringent material, the beam is broken into two polarized components which travel at different speeds and vibrate at right angles to each other. This results in double refraction and the two light components emerge as parallel beams of polarized light. A convenient way to identify a liquid crystalline material is to test it for birefringence; all other known birefringent compounds are solids.

Using a microscope that will admit only polarized light, it can be shown that a smectic liquid crystal behaves like a three dimensional crystal such as quartz. The velocity of the light transmitted perpendicular to the layers is less than that transmitted parallel to the layers. Structures of this type are known to be optically positive. This feature is a consequence of the molecular array, not of the properties of the molecules or of the structure of small regions.

The smectic phase between a glass slide and a coverglass or between the surfaces of some plastic material will show twisting of the smectic layers producing optical designs exhibiting the shapes of ellipses and hyperbolae. These designs have been described as focal conics and represent optical discontinuities in the system. Each confocal group (domain) has

its layers of molecules ordered in a way such that their surfaces form a series of cyclides.

The whole sample in the specimen is split up into such domains; each layer belongs simultaneously to several domains. This gives rise to polygonal structure, in which case the system splits up into pyramidal and tetrahedral blocks, each pyramidal block having several domains. The tetrahedral blocks contain the smectic layers connecting the domains in the pyramids.

Smectic textures can be produced in the form of stepped design (Grandjean terraces) if the substance is melted on a clean flat surface. The thickness of the steps is visible, but it would appear that the thickness approximates a multiple of the length of the molecule.

Like the smectic liquid, the nematic liquid is optically positive. The nematic liquid is generally not optically active unless there is asymmetry in the molecule. However, the optically inactive nematic liquid can be made to rotate the plane of polarization of light if the glass plates between which the material is placed are twisted. The deformation of the structure by adhesion to the glass surfaces causes the optical activity, thus generating a cholesteric structure.

The cholesteric liquid is optically negative. Light entering the structure perpendicular to the molecular layers has the maximum velocity which is in complete contrast to the nematic and smectic liquids.

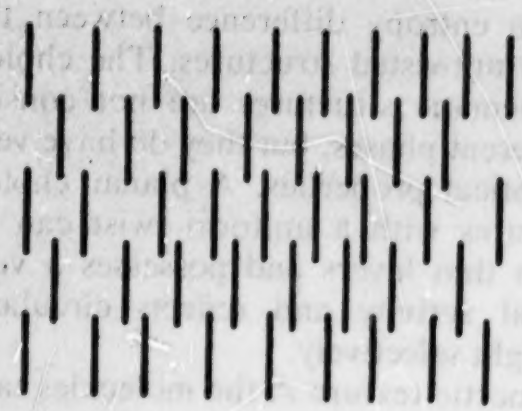
Optical Rotation: In many ways the cholesteric structure resembles the nematic structure. However, the unique architecture of the cholesteric liquid gives rise to a number of optical properties which are not exhibited by the nematic liquids. As an example, linearly polarized light transmitted perpendicular to the molecular layers will have the direction of its electrical vector rotated progressively to the left along a helical path. The plane of polarization of the light will be rotated to the left through an angle proportional to the thickness of the transmitting material. Materials which possess this property are said to be optically active. Certain structures of quartz will rotate polarized light, the extent being dependent to some degree on temperature and to a greater degree on the wavelength of the light. At 20°C, a one millimeter section of quartz will rotate light of a wavelength of 656 millimicrons (red) 17.25° while the same sample will rotate light of a wavelength of 448 millimicrons (blue) 39.24°. A one millimeter section of an optically active substance that shows the cholesteric liquid (-)-2-methylbutyl-4-(cyanobenzylideneamino) cinnamate at 75°C rotates light of a wavelength of 658 millimicrons (red) 5300° and of a wavelength of 452 millimicrons (blue) 27,650°. No other substances are known which compare to liquid crystals in their capacity to rotate polarized light.

Dichromism: The cholesteric liquid exhibits dichromism, that is, one of the polarized components of light is absorbed in the structure much more strongly than the other. In other words, the ordinary light is separated into two components one with electric vector rotating clockwise and the other vector rotating counter-clockwise. The kind of material determines whether one of these components is transmitted or reflected. It is this property of dichromism that gives the cholesteric liquid its characteristic irridescent color. The colors which this structure exhibit are dependent upon the temperature, the material and the angle of the incident radiation.

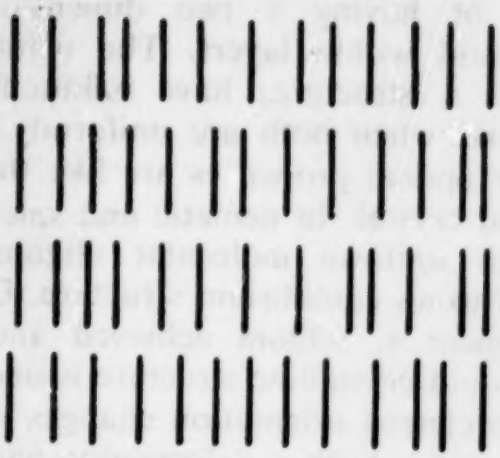
STRUCTURE OF THERMOTROPIC LIQUID CRYSTALS

For many years three classes of thermotropic liquid crystals have been accepted, namely nematic, smectic A and cholesteric. Recent observations have shown that the cholesteric structure is only a special case of the nematic. This reaffirms what Friedel suggested about 45 years ago. (17)

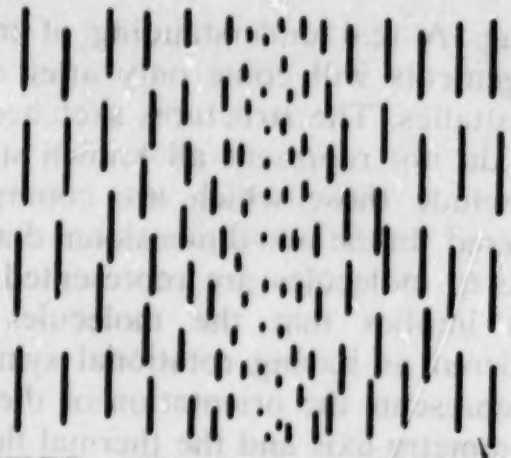
The molecular arrangements in two dimensions of the different thermotropic liquid crystals may be represented schematically as sketched in Figure 6. It should be understood that these schematics present the best suggestions we can give at this time on molecular



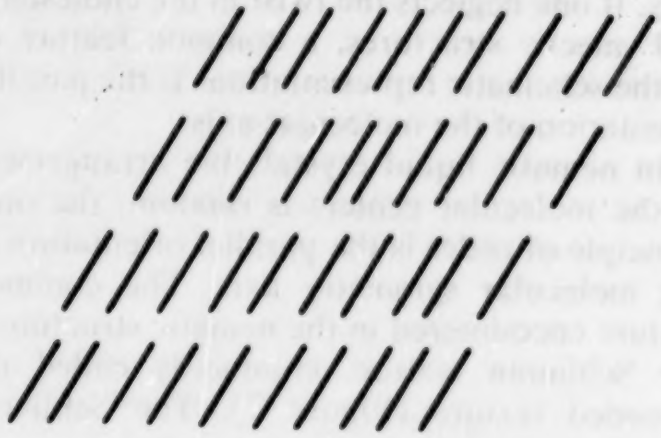
NEMATIC STRUCTURE
(A)



SMECTIC STRUCTURE A
(C)



TWISTED NEMATIC STRUCTURE
(CHOLESTERIC STRUCTURE)
(B)



TILTED SMECTIC STRUCTURE
(D)

TWISTED SMECTIC STRUCTURE
(E)

Figure 6. Schematic representation of several liquid crystalline structures. (A) Nematic Structure; (B) Twisted Nematic Structure or Cholesteric Structure; (C) Smectic Texture A; (D) Tilted Smectic Structure; and (E) Twisted Smectic Structure.

packing. A real understanding of molecular arrangements will come only after extensive x-ray studies. The structures sketched in Figure 6 do not represent all known structures, but include those which are commonly encountered. In the two-dimensional diagrams in Figure 6, molecules are represented by lines which implies that the molecules can be considered as having rotational symmetry; a line represents the orientation of the molecular symmetry axis and the thermal fluctuation of the molecule is neglected in the drawings. The alignment of the line represents the position of the molecular axis with respect to the plane of the drawing. Molecules aligned perpendicular to the plane are represented by dots. If one neglects the twist in the cholesteric and smectic structures, a common feature of all the schematic representations is the parallel orientation of the molecular axis.

In nematic liquid crystals the arrangement of the molecular centers is random; the only principle of order is the parallel orientation of the molecular symmetry axis. The common texture encountered in the nematic structure is the Schlieren texture, commonly called the threaded texture (Figure 7). The Schlieren

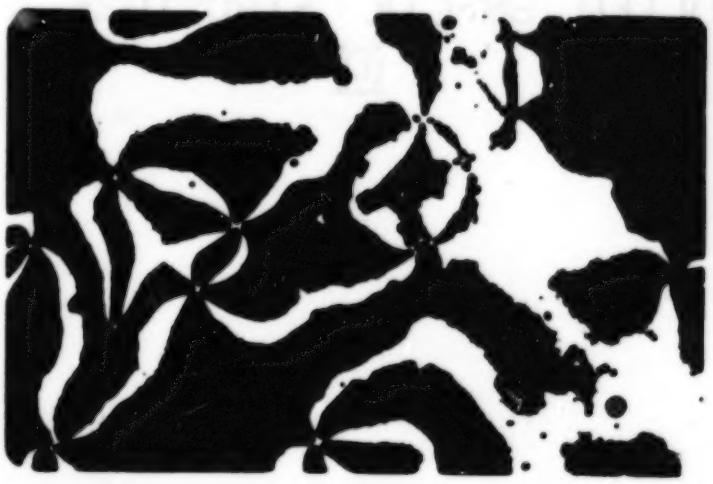


Figure 7. The thread-like pattern of a nematic liquid crystal. The compound is terephthal bis-(p-amino-n-butylbenzene). Magnification x22 between crossed nicols.

texture shows continual movement. The cholesteric structure, like the nematic, has the parallel orientation of the molecules. It may be considered as a twisted-nematic structure. There is no entropy difference between the twisted and untwisted structures. The cholesteric and nematic structures are not considered as different phases, but they do have very different optical properties. A planar cholesteric structures with a uniform twist can be prepared in thin layers and possesses a very nigh optical activity and reflects circularly polarized light selectively.

In the smectic texture A the molecules take on a layer arrangement which gives this structure an additional degree of order over the nematic structure. Within the layers the molecules are randomly positioned so that one may think of having a two dimensional isotropic liquid within layers. The nematic and smectic A structures have infinite-fold symmetry and when both are uniformly oriented, their optical properties are like those of a uniaxial crystal. In nematic and smectic A structures uniform molecular alignment corresponds to an equilibrium structure. Uniform alignment is seldom achieved and a deformed liquid crystalline structure is one in which the preferred orientation changes with position in space. Such a deformation causes the discontinuities which appear as threads in nematic structures (Figure 7). Discontinuities also appear in smectic textures (Figure 8).

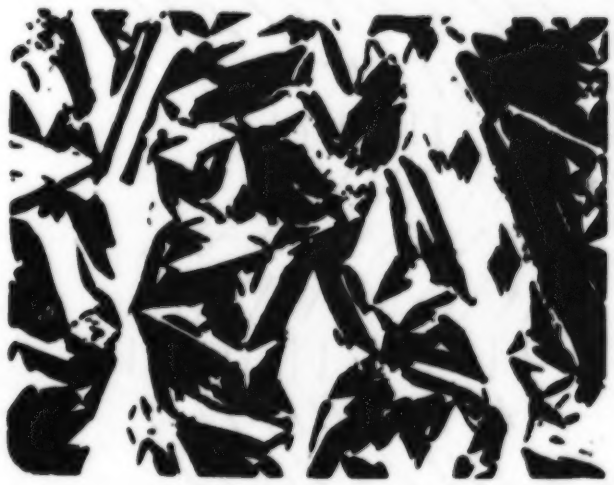


Figure 8. The focal conic structure of a smectic A liquid crystal. Notice the folding of the layers to give the conic designs. The compound is terephthal bis-(5-amino-2-n-butoxypyridine). Magnification x22 between crossed nicols.

Before leaving a discussion of smectic structures we might mention that other patterns of molecular arrangements can be suggested. Of these possibilities we mention the tilted smectic and the twisted smectic. These are sketched in Figure 6 (D) and 6 (E). The tilted smectic structure has been known for many years. It does not have ordering of a higher order than the smectic texture A. Smectic A may be considered a special case of the tilted structure with the tilt angle gone. The tilted smectic has only one plane of symmetry and a two-fold summetry axis perpendicular to it. This structure is optically biaxial. Tilted smectic structures are as easily twisted as nematic structures. Enantiomorphs may result in structures with a spontaneous twist as is common with cholesteric liquid crystals.

THEORETICAL ASPECTS OF LIQUID CRYSTALLINE STRUCTURES (A MODEL STRUCTURE)

Two theories to explain the structure of nematic liquid crystals have had considerable support with the Continuum Theory receiving far more attention recently than the Swarm Theory. The Swarm Theory, in brief, states that the molecules in a nematic liquid crystal form aggregates in swarms containing on the average 10^5 molecules. The molecules within the swarm lie parallel to one another. The directional components of the interaction between swarms is small, so the orientation of the axes of the swarms to one another is random. An external force (e.g. magnetic or electric field) can impose a uniform orientation. The swarms have a limited lifetime and molecules in a swarm can exchange with the isotropic environment or with those of other swarms. The strong light scattering properties of nematic liquid crystals can be easily explained by the Swarm Theory. The nematic structure has been found to be more continuous than expected when the Swarm Theory was proposed; thus, the concept of the theory has to be altered to accommodate the findings or a new theory has to be proposed.

The Continuum Theory is based on the assumption that at every position in an undisturbed liquid crystal there is a preferred direction for the orientation of the longitudinal axes of the molecules. This preferred direction is supposed to change continuously with position, except possibly at special surfaces where the preferred direction is no longer defined. An example of a special surface where there is a discontinuity is the thread in the nematic structure. The Continuum Theory can be applied to cholesteric and smectic structures as well as to the nematic one.

The assumptions of the Continuum Theory lead one to expect that liquid crystals have elastic flexible structures and that the deformation energy can be calculated with the aid of elastic constants. This energy has been calculated for one nematic structure from equations derived from the fundamental assumptions of the Continuum concept. The theory has possible applications in predictions for viscometry and for propagation of orientation waves. Unfortunately, no quantitative data are available on wave speeds. Data on shear flow are scarce and thus the results of the Continuum Theory are still in need of rigorous testing.

APPLICATIONS

Two properties of liquid crystals that have been exploited thus far for practical uses are color change as a function of temperature for the cholesteric type and response of the nematic structure to an electrical field. One can call the first type of application thermal mapping or thermography.

Some properties of the cholesteric state which control its uses

The cholesteric structure generated by cholesteric esters is dependent very much on the geometry of the molecule. What we say about the geometry of the cholesteric esters is not necessarily applicable to non-cholesteric molecules that form the cholesteric structure. The formula for cholesteryl nonanoate is given in Figure 5 and a proposed packing pattern for

the molecules is shown in Figure 9. The pattern in Figure 9 is like the one in Figure 6 but in more detail. You will notice that the ring system in cholesterol is essentially planar but the ester chain, the methyl groups, and some of the hydrogen atoms on the rings are not in the plane of the rings. Notice that the long axes of the molecules in any two given planes are slightly oriented to one another to accommodate the units that are attached to the rings (see Figure 9). This staggered packing (follow the dots in the ellipses which represent molecules) gives a helical pattern which accounts for some of the interesting optical properties of cholesteric esters.

Mixtures of cholesteric liquid crystals can be used to develop applications. Such mixtures may involve two or more cholesteric esters, a cholesteric ester and a nematic phase and a cholesteric ester and a dye. These combinations make a very large variety of liquid crystalline materials that change color over a wide range of temperatures.

At a given temperature the wavelength of maximum scattering depends on the angles of incidence and scattering. In many respects the

Figure 9. Schematic design representing molecular packing in a cholesteric structure. Note the helical design.

cholesteric structure behaves as a multiple-layer interference filter but, because of the internal structure, the higher orders are suppressed. The scattering of visible radiation by the cholesteric structure is analogous to the scattering of x-ray from crystals. At a given temperature, the wavelength of maximum reflection as a function of angle may be represented by the following equation:

$$\lambda_{max} = \lambda_n \cos \tfrac{1}{2} [\sin^{-1} (\tfrac{n}{n_l} \sin\theta_l) + \sin^{-1} (\tfrac{n}{n_l} \sin\theta_s)]$$

where λ_{max} = wavelength of maximum scattering

λ_n = wavelength of maximum scattering for normal incident radiation

n = refractive index of the medium around the sample

n_l = refractive index of the liquid crystal

θ_l = angle of incident radiation

θ_s = angle of the scattering radiation.

The wavelength of maximum scattering of radiation from a cholesteric structure will change with temperature or with materials (certain chemicals) which intrude into the liquid crystalline structure. The explanation of this change is seen by looking at Figure 9. The change in pitch brought about by change in temperature or by intrusion of a chemical will cause a change in the wavelength of maximum scattering. The distance between

two aligned axes is $d = P\phi/180 = \frac{\lambda\phi}{360}$ where d = plane spacing, λ = wavelength of scattered light, ϕ = angle between adjacent planes in degrees, and P = pitch. If the spacing of planes in the cholesteric structure is about 3Å, the spectrum of the visible radiation can be transversed with an angular shift of 7 minutes of arc.

In using liquid crystals in thermal mapping, a number of factors should be considered. These may be presented briefly as follows:

The size of the object to be measured must be larger than the resolution of the cholesteric structure. The practical limit on the size of the spot to be measured is 0.02 mm.

The heat capacity of the material to be measured must be greater than that of the liquid crystal.

Obviously, the temperature to be measured must be in the range of available liquid crystalline materials. The temperature ranges of cholesteric esters or mixtures is from about -30° to 310° C. The most practical temperature range is from 0° to 100° C.

The thermal change to be measured must be slow enough to allow the cholesteric liquid crystal to follow. The time constant of rate of change of color with temperature is of the order of 0.1 sec. This time constant does not create a problem for visual observation but must be considered if quantitative information is to be obtained from photography.

The background against which the colors are to be observed should be black. The cholesteric liquid scatters light selectively thus making it essential to absorb the light which is not scattered.

The surface to which the liquid crystal is applied should be free of materials that dissolve in the liquid crystal. Impurities may have pronounced effects on the behavior of cholesteric liquid crystals.

Some uses of liquid crystals

In the electronics industry one may classify the objects to be tested into large system mapping (15 cm² and larger), subassemblage mapping (0.1 to 15 cm²) and components mapping (0.1 cm² to micron size). The two prime purposes for thermal mapping in the electronics industry are to obtain temperature distributions of operating devices and to identify heat-producing malfunctions. The first of these uses identifies heat flow and temperature distribution patterns as well as the spatial power dissipation of operating devices. The second use is diagnostic, pointing out existing or potential failures as well as structural characteristics of localized heat sources or conduction paths.

Component mapping is related to such objects as integrated and monolithic circuits. These objects may approach micron size with a high-element density. The use of cholesteric liquid crystals to study these objects has made most of the conventional methods obsolete. The major difficulty in the use of liquid crystals in component mapping is to obtain uniform coatings of the required thickness. With a little practice the art can be easily mastered. The procedure for carrying out these tests have become quite standard and may be found in a paper by Lauriente and Fergason written about two years ago. (18)

Cholesteric liquid crystals have been found useful in the measurement of surface temperatures in aerodynamic designs. The remarkable sensitivity to temperature change has made it possible, for the first time, to observe some of the finer details in boundary layer flow such as occur in transition regions from laminar to turbulent. Small shock waves impinging on the surface can also be detected. The major practical application of liquid crystals in aerodynamic studies is the delineation of

laminar and turbulent regions on aerodynamic designs. Since liquid crystals show reversible color changes, another interesting application would be the investigation of slow transient surface phenomena.

Liquid crystals have been encapsulated and thus are protected from air decomposition and from dust particles which adversely affect their scattering properties. (19)

The use of cholesteric liquid crystals as an investigative and diagnostic tool in medicine has become rather widespread in the past several years. A couple of examples will be given. Observation of skin temperature changes following blocks of the sympathetic nervous system enables physicians to determine if neurological and vascular pathways are open. Skin infections and malignant skin tumors may be detected and mapped by use of cholesteric liquid crystals. Their temperature is invariably greater by as much as two or three degrees centigrade than the surrounding skin. By permitting the physician to monitor an extended area of the skin circulatory patterns, infections and tumors can be detected and mapped more effectively than with point measurements using thermocouples and thermistors.

Advantage has been taken of the response of nematic liquid crystals to an electric field. This property was well defined by Brown, et al. (20) The property has been developed by RCA and prototypes of devices have been built. These include a numeric indicator, an all-electric clock with no moving parts, and an electronically controlled window.

In the laboratory liquid crystals have been used as stationary phases on a chromatography column. Effective separation of the xylenes on such a column illustrates one application of this emerging field of chromatography. Nematic liquid crystals are quite useful as solvents for high resolution nuclear magnetic resonance studies. Accurate molecular structures of solute molecules have been obtained by analysis of the nmr spectra of the solutes in nematic liquid crystals. As an additional benefit one can find absolute values of indirect spin-spin couplings and their assignment to nuclear pairs.

Liquid crystals in microwave detection

Liquid crystals have brought real time into the measurement of microwave intensity. A broadband microwave detector that displays color as a function of microwave intensity has been developed. (21) The detector has been described as having good resolution and is efficient. It can be used to plot near-field antenna patterns and mode patterns in complex waveguides and resonators and to measure impedance and power by detecting standing waves and power-density patterns in open transmission lines. It has been suggested that such a detector may be useful in microwave holography.

The detector is simply a thin Mylar membrane with a thin metal film deposited on one side of the membrane which is then coated with the liquid crystal. The size of the Mylar film depends on the experiment. The microwave passes through the membrane and sets up currents in the metal film. The energy transferred to the metal film heats it throughout in proportion to the amount of energy absorbed. The color developed in the liquid crystal depends on the temperature and a distinct color pattern, identifying the intensity of the microwave, develops.

The experiment involves the preparation of a Mylar membrane (about one mil) with a metal coating on one side and a film of liquid crystal on top of the metal. The cholesteric liquid crystal shows the complete visible spectrum in a range of about 4°C. The resistivity of the membrane was approximately 400 ohms over the area studied. The solution of the liquid crystal is prepared in a volatile solvent (e.g. petroleum ether); the concentration is about 10% by weight. Different liquid crystal systems can be used to show color changes in 4°C ranges from 0° to 100°C.

After the membrane is prepared it is placed about one inch from a radiating x-band

waveguide. Energy of about 200 milliwatts (5 x 10^{-3} cal./sec.) radiating from the waveguide gave distinct oval concentric bands on the membrane with a color pattern defining the pattern of the microwave, the color characterizing the intensity of the microwave. The color change from red to blue is equivalent to a power spread of about 7 decibels but this value can change with liquid crystal composition. The concentric pattern can be expanded or contracted by adjusting the amount of power from the waveguide. The membrane's efficiency can be increased by impedance matching. A given color on the film results from a specific power density. One can calibrate the film by making incremental changes in the power density and noting the color related to each power setting.

Augustine has proposed that a microwave fluoroscope could be made quite easily. **(21)** The instrument could be used to find internal flaws or changes in density or thickness of materials that are translucent to microwaves.

Using two collimating antennae opposite each other essentially plane waves are radiated. The plane waves, traveling in opposite directions, create standing waves having troughs and peaks in planes perpendicular to the direction of propagation. If a membrane is placed in the trough of the standing wave, the energy will be a minimum and give a color corresponding to a minimum temperature. If the membrane is placed on the peak of the wave, the color of the liquid crystal will show a color characteristic of the higher temperature.

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from page 23

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